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The following information is taken from the documents submitted by the applicant.

- (54) Method for Production of Polyurethanes from Renewable Raw Materials
- (57) Method for production of polyurethanes by reacting of polyisocyanates (A) with compounds containing isocyanate-reactive groups (B), characterized in that (A) and (B) are made from renewable raw materials.

Specification

The invention concerns a method for production of polyurethanes, whose building blocks are made from renewable raw materials.

Polyurethanes have long been known and have diverse uses. Their production occurs by reaction of polyfunctional isocyanates with H-functional compounds, especially polyols. The raw materials for production of polyurethane are mostly of petrochemical origin. The drawback to most polyurethanes, especially polyurethane foams and casting compounds, is their poor recyclability. Since the mentioned substances have no thermoplastic properties, only chemical and thermal recycling is possible for them. Thermal recycling is questionable for ecological reasons. A number of methods are known for chemical recycling. Thus, DE-A-42 34 335 describes a method for production of glycolysis polyols from polyurethane foams. However, such methods can hardly be used for polyurethane containing fillers, for example, two-dimensional molded parts with fibers as reinforcement, since the reinforcement remains as insoluble residue in the reaction mixture and has to be removed in a costly manner.

A biological decomposition of polyurethanes is possible, for example, by composting. However, the aromatic isocyanates which are conventionally used will produce aromatic amines as decomposition products. These are carcinogenic and therefore preclude a specific biological decomposition of polyurethanes.

The use of renewable raw materials in the production of polyurethanes is known.

Thus, most natural oils contain double bonds as the functional groups, which cannot be made to react directly with isocyanates. However, it is possible to oxidize these double bonds to epoxy groups. The epoxy groups can then be opened and hydroxyl and amino groups can be introduced by this ring-opening step.

DE 10 42 565 describes the epoxidation of fatty acids with performic acid.

US 3 475 499 describes the ring-opening reaction of epoxy alkanes with water and ethylene glycol.

DE 32 46 612 describes modified triglycerides with epoxide, ether and hydroxyl groups by partial ring opening of epoxidated fatty acid esters with alcohols.

DE 39 35 127 describes ester polyols obtained by the ring-opening reaction of epoxidated esters and alcohols with carboxylic acids.

EP 113 798 describes the production of polyfunctional oleochemical polyols by reaction of epoxidated fatty alcohols with polyfunctional alcohols or phenols and possibly further reaction with EO/PO.

DE 41 25 031 and DE 42 03 077 describe methods for preparation of hydroxylated fatty acid compounds by reaction of epoxy fatty acid derivatives with active hydrogen-containing

compounds in the presence of acid-activated aluminas and/or silicates and/or activated charcoal. The ring opening is conducted, again, with polyethylene glycol.

Polyols isolated directly from replenishable raw materials can often be used for production of polyurethanes after simple chemical modification steps. Sucrose, sorbitol, glycerine, Ricinus oil and alkyl glucosides, alone or in mixture with other co-initiators, are reacted with alkylene oxides to polyetherols of the most diverse functionality and OH number, each of them specially optimized for production of hard to soft and high to low density polyurethanes (see Oertel, *Plastics Handbook Volume 7: Polyurethanes*, Chapter 3.1: Polyols, Hanser Verlag, 2nd ed. 1983).

Other polyols obtained from renewable raw materials, such as glycerine or Ricinus oil, already have in their natural form hydroxyl groups reactive to isocyanates and are immediately suitable for production of polyurethanes.

Isocyanates made from replenishable raw materials are likewise known.

Stanford in *Amer. Chem. Soc. Symp. Series*, Vol. 385 (1989), Chapter 30: Polyurethanes from Renewable Resources, describes the production and processing into polyurethanes of di- and polyisocyanates similar to MDI, starting from furfural, which is available from renewable raw materials.

EP 369 590 describes the use of dimerisocyanate obtained from dimer fatty acids for production of polyurethanes.

The production of isocyanates from amino acids and the further reaction into polyurethanes for films, coatings, adhesives, casting compounds and binders with especially improved light stability has long since been known. Thus, FR 1 351 368 describes the production of carboxyalkylisocyanates and US 3 281 378 the further reaction into compact polyurethanes. JP 53 135 931, JP 57 077 656, JP 60 222 450 and JP 61 053 254 describe the production of (lysine ester) triisocyanates.

Many other patents describe the use of lysine diisocyanate as one possible (aliphatic) isocyanate alongside other (aliphatic) isocyanates for production of polyurethane coatings, paint, adhesives, packaging films, sealing materials, duromers and foams. Thus, DE 36 30 667 describes the production of paint and EP 23 934 and US 4 247 675 the production of weatherproof coatings, EP 304 083 the production of adhesives, JO 3 239 715-A the production of moisture and temperature-resistant soft foams.

Storey, in *Polymer Composites*, 1993, 14, 17-25, describes the production of biodegradable and bioresorbable polyurethanes from lysine diisocyanate and polylactide polyols. The decomposition products of these polyurethanes are lysine, lactic acid, glycerine and CO₂ and thus are natural nontoxic substances.

WO 8905-830-A describes biodegradable and bioresorbable material for medical sutures based on lysine diisocyanate.

DE 40 06 521 describes polyurethanes as coatings or primary material for orally administered medicines based on lysine isocyanate.

US 4 018 636 and US 4 293 352 describe polyurethanes based on lysine isocyanate as binder for explosives, which are stable with respect to water, but can be broken down in aqueous acids or ammonia to recover the explosives.

EP 327 031 describes the use of lysine diisocyanate as an aliphatic isocyanate for production of PUR coatings.

The basic problem of the invention was to provide polyurethanes which are biodegradable, without giving rise to toxic or environmentally harmful decomposition products.

The object of the invention is a method for production of polyurethanes, characterized in that both the polyol and the isocyanate components are made from renewable resources and the polyurethanes prepared according to this method. The polyurethanes of the invention can be either compact or foamed. Preferred are foamed polyurethanes, especially molded polyurethane sheets. The invention is used with special advantage for foamed molded polyurethane sheets with natural fibers as reinforcement agent. The benefits consist, first, in that the natural fibers are better wetted by the polyurethane systems based on renewable resources and therefore the molded bodies are very homogeneous in their construction. Secondly, the entire molded piece is entirely biodegradable.

The production occurs by the usual and known methods as are employed in polyurethane chemistry.

The use of the invented polyurethanes is in the same applications as the conventional polyurethanes.

The content of renewable resources in the polyurethanes can be greater than 90 wt. %. The remainder can consist of polyols based on petrochemical building blocks, such as polyesterols from the reaction of aliphatic polycarboxylic acids with aliphatic alcohol components, polyether alcohols from the reaction of H-functional compounds with lower alkylene oxides, or the often used low-molecular chain lengthening and/or cross linking agents.

The following in particular can be said about the polyurethane components based on renewable resources:

As the isocyanate component, one preferably uses those obtained from the corresponding amino acids. The preparation of these isocyanates is usually done by esterification of the acid groups and phosgenation of the amino groups of the amino acids. Preferably used amino acids are dimer fatty acid diisocyanate, lysine or its biuret- or triisocyanate derivatives, especially lysine.

As the polyol components, one can use hydroxyl-functional natural substances, such as Ricinus oil or tall oil, whose use in production of polyurethanes is familiar.

It is also possible to use polyols from reaction products of natural substances. For example, they can be alkoxyated, hydroxyl-functional natural substances, especially sugars such as sucrose, sorbitol, or mannitol, or also glycerine polyetherols.

It is also possible within the meaning of the invention to use low-molecular hydroxyl-functional natural substances like glycerine or sugar alcohols as chain lengthening or cross linking agents.

The use of fatty acid esters modified by epoxidation and subsequent ring opening is also possible.

Especially advantageous are molded bodies, particularly sheetlike shapes, with natural fibers as the reinforcement. The polyurethane systems made from renewable raw materials result in a better wetting than the conventional polyurethane systems made from aromatic polyisocyanates and long-chain polyalkoxypolyols. The wastes from such products can be shredded and composted.

Another benefit of polyurethanes based on amino acid polyisocyanates is their color stability. While polyurethanes made from aromatic polyisocyanates turn yellow even after a short time, the polyurethanes of the invention do not change color, even after a long time.

The invention will be explained more closely by the following examples:

Example

Polyol component:

Ricinus oil: 36.00 g

Glycerine: 30.00 g

Sovermol Pol 930: 30.00 g (Henkel Co., OH number 195)

Water: 2.50 g

Formrez UL 32: 1.00 g (Witco Co.)

Silicon B 8404: 0.50 g (Goldschmidt Co.)

Isocyanate component: Lysine ethylester diisocyanate (2,6-diisocyanate ethyl hexanoate, NCO content: 37.2%)

Mix ratio (polyol/isocyanate component) = 100:170

In a 1000 ml plastic flask, polyol and isocyanate component are intimately mixed for 30 seconds and poured out into a second flask.

Properties

Starting Time: 25 seconds

Starting Time: [sic] 25 seconds

Setting Time: 40 seconds

Rise Time: 60 seconds

Density: 48 g/l

The foam is very white and remains unchanged after 30 days of being in sunlight. It is decomposed by microorganisms into safe residues.

Comparison Example

Polyol component:

Ricinus oil: 36.00 g

Glycerine: 30.00 g [handwritten notes illegible]

Sovermol Pol 930: 30.00 g (Henkel Co., OH number 195)

Water: 2.50 g

Formrez UL 32: 1.00 g (Witco Co.)

Silicon B 8404: 0.50 g (Goldschmidt Co.)

Isocyanate component: Luprant M20 (polymeric diphenyl methane diisocyanate
NCO content: 31.3%, Viscosity 200 mPas)

Mix ratio (polyol/isocyanate component) = 100:202

In a 1000 ml plastic flask, polyol and isocyanate component are intimately mixed for 30 seconds and poured out into a second flask.

Properties

Starting Time: 18 seconds

Setting Time: 35 seconds

Rise Time: 54 seconds

Density: 43 g/l

The foam is beige and turns brown after 30 days kept in sunlight. It is broken down by microorganisms into residues which may contain aromatic amines.

Patent Claims

1. Method for production of polyurethanes by reaction of polyisocyanates (A) with compounds which contain isocyanate-reactive groups (B), characterized in that (A) and (B) are prepared from renewable raw materials.
2. Method per Claim 1, characterized in that (A) is made from amino acid esters.
3. Method per Claim 2, characterized in that (A) is made from lysine acid esters.
4. Method per Claim 1, characterized in that (B) is made from plant oils.
5. Method per Claim 1, characterized in that (B) are plant oils containing hydroxyl groups or derivatives thereof.

6. Method per Claim 1, characterized in that the percentage of renewable raw materials in A+B is at least 90 wt. %.
7. Polyurethanes which can be prepared per Claim 1.
8. Polyurethanes per Claim 7, characterized in that they are foamed polyurethanes.
9. Polyurethanes per Claim 7, characterized in that they contain natural fibers as reinforcing agent.

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